

QUANTITATIVE DESCRIPTION OF THE CHANGES
IN THE ACID-BASE PROPERTIES OF BROMOCRESOL GREEN
IN THE PRESENCE OF SUBMICELLE AND MICELLE
CONCENTRATIONS OF CATIONIC TENSIDE—SEPTONEX

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The effect of cationic surface-active substances — tensides — on the acid-base and optical properties of anionic organic analytical reagents was studied by spectrophotometric methods on the example of bromocresol green with Septonex in the submicelle and micelle tenside concentration regions. The acid-base properties of bromocresol green under the given experimental conditions depend on the concentrations of the tenside and reagent and on the type and concentration of the inert electrolyte. Changes in the conditional dissociation constant of the reagent were quantitatively described by equations that were derived from the relationships for the dissociation constant of the acid-base transition of the reagent LH/L^- , the equilibrium constant for formation of the stoichiometric ion-associates between the tenside T^+ and the anionic acid-base form of the reagent L^- or the anion of the inert electrolyte X^- and the equilibrium constant for formation of the polymeric micelle aggregates $(T^+)_n$. The experimental values of the conditional dissociation constants for bromocresol green for various tenside or inert electrolyte concentrations agree in good agreement with these theoretically derived relationships.

The presence of submicelle and micelle concentrations of high-molecular surface-active substances — tensides — leads to marked changes in the physical and chemical properties of solutions and reagents and affects the course of chemical reactions and catalytic processes^{1,2}. Interaction of tensides with metal chelates of coloured organic analytical reagents leads to an increase in the sensitivity and colour contrast in spectrophotometric methods of determining polyvalent elements, with a sensitivity 2–10 times higher than that for the corresponding binary system and a colour contrast of between 80 and 250 nm (refs^{3–5}).

The interaction between coloured organic reagents (L) and ionic and nonionic tensides (T) at low concentration excesses of tenside ($c_T/c_L < 10$) and low overall tenside concentrations ($c_T \cdot 10^{-4} \text{ mol l}^{-1}$) leads to formation in water of poorly soluble ion-associates of the tenside with the reagent $\{L \cdot T_n\}$ that can be readily extracted into organic solvents. These ion-associates all have precisely defined stoichiometric compositions ($\{L^- \cdot T^+\}$, $\{L^{2-} \cdot 2 T^+\}$, etc.). The number of tenside molecules is determined by the overall charge on the organic reagent molecule^{6–11}.

The ion-associates are solubilized at higher concentration excesses of tenside and higher overall concentrations ($c_T/c_L > 10$, $c_T > 10^{-4} \text{ mol l}^{-1}$).

Bonding of the tenside molecule to a donor atom or group with an isolated π -electron system ($-\text{SO}_3^-$, *etc.*) does not lead to much change in the absorption spectrum compared to that of the reagent alone⁹⁻¹¹. When the tenside is bonded to a donor atom or group with a delocalized π -electron system in the overall π -electron system of the reagent molecule ($-\text{OH}$, $-\text{COOH}$, *etc.*), then new absorption band appears in the spectrum of the ion-associate at longer or shorter wavelengths or the absorption band of the reagent is shifted into the long wavelength spectral region⁹⁻¹¹.

The acid-base properties of the reagent change during formation of the ion-associate. At a constant reagent concentration ($c_L \approx 10^{-5} \text{ mol l}^{-1}$), the shift in the dissociation equilibrium to the acidic or alkaline region depends on the type and concentration of tenside and on the type and concentration of inert electrolyte (ionic strength of the solution)¹⁰. At a constant tenside concentration and given kind and concentration of inert electrolyte, the change in the acid-base equilibrium depends on the overall reagent concentration^{10,12}. These changes are most marked in the region of submicelle tenside concentrations. The changes in the acid-base properties of the reagent are small or zero in the concentration range close to the critical micelle concentration of the tenside c_K (ref.⁸⁻¹¹).

The character of the interaction between the tenside and the coloured organic reagent or its metal chelate is not quite clear. These interactions have been explained by formation of ion-pairs or ion-associates of the reagent with simple tenside molecules⁹⁻¹⁴ or micelle aggregates¹⁵. These effects have also been described by sorption of the dye molecule and its ion-associates with the tenside or metal chelate on the surface of the micelles¹⁶⁻¹⁸ or entrance into the internal micelle structure^{19,20}.

Most of these considerations remain qualitative or semi-quantitative without quantitative relationship and equations that would express the shift in the acid-base equilibrium of the reagent and changes in the conditional equilibrium constants or kinetic rate constants in dependence on the experimental conditions (tenside and inert electrolyte concentration, *etc.*).

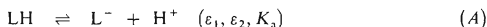
Funasaki²¹ published some of the first quantitative relationships describing the interaction of organic reagents in the submicelle concentration region, describing interaction between the tenside and organic dye in terms of electrostatic theory and ion-exchange models. Both these models satisfactorily describe the effect of the tenside concentration on the shift in the acid-base constant of thymol blue and on the rate constant of basic hydrolysis of *p*-nitrophenyl lactate in micellar solutions.

This work considers some experimental factors that affect the formation of ion-associates of organic reagents in tenside solutions and the shift of the acid-base equilibria of organic dyes. Quantitative relationships are derived to describe the dependence of the shift in the conditional dissociation constant of the acid-base equilibria of weak monobasic acids on the tenside concentration, type and concentra-

tion of strong inert electrolyte or ionic strength of the solution. Theoretical conclusions are tested using some experimental data obtained in study of the acid-base and optical properties of bromocresol green in a wide concentration range of Septonex and Cl^- , NO_3^- , ClO_4^- and SO_4^{2-} anions.

THEORETICAL

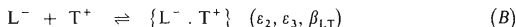
It will be assumed for simplicity that the analytical organic dye exists in the studied acidity interval in only two acid-base forms, LH and L^- , with molar absorption coefficients of ϵ_1 and ϵ_2 . The ratio of the equilibrium concentrations of the two acid-base forms is controlled by acid-base equilibrium (A) and dissociation constant K_a :



$$K_a = [\text{L}][\text{H}]/[\text{LH}] \quad (I)$$

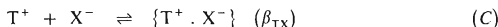
(charges are omitted in the relationships for simplicity).

In the concentration region where the cationic tenside (generally alkyl ammonium) forms an ion associate $\{\text{L}^- \cdot \text{T}^+\}$ with molar absorption coefficient ϵ_3 and stability constant β_{LT} with the anionic acid-base form L^- according to equilibrium (B)



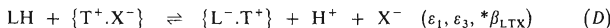
$$\beta_{\text{LT}} = [\text{L} \cdot \text{T}]/[\text{T}][\text{L}]$$

and the ion-pair of the tenside is simultaneously associated with the counter ion X^- (Cl^- , Br^-) according to the equilibrium



$$\beta_{\text{TX}} = [\text{T} \cdot \text{X}]/[\text{T}][\text{X}] \quad (3)$$

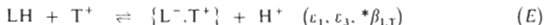
The chemical reaction of the reagent with the tenside can be understood as competing equilibrium (D) with reaction equilibrium constant $^*\beta_{\text{LTX}}$:



$$^*\beta_{\text{LTX}} = [\text{L} \cdot \text{T}][\text{H}][\text{X}]/[\text{LH}][\text{T} \cdot \text{X}] \quad (4)$$

Under the usual experimental conditions, where the tenside concentration c_{T} is several times higher than that corresponding to the concentration of the organic dye, c_{L} ($c_{\text{T}} \approx 10^{-4} \text{ mol l}^{-1}$, $c_{\text{L}} \approx 10^{-5} \text{ mol l}^{-1}$) and the ion-pair of the tenside with the

counter ion $\{T^+, X^-\}$ is completely dissociated ($R_4N^+Cl^-$, $R_4N^+Br^-$), reaction equilibrium (D) and its equilibrium constant can be written in simplified form



$${}^* \beta_{LT} = [L \cdot T][H]/[LH][T]. \quad (5)$$

For a given type of reagent, equilibrium constant ${}^* \beta_{LT}$ of reaction (E) depends on the overall tenside concentration and equilibrium constant for formation of the corresponding ion-pair of the anion of the reagent with the tenside in the sense of the formal dissociation equilibrium of the acid-base form of the reagent LH, forming ion-pair $\{L^-, T^+\}$ and dissociation of one proton, according to the relationships

$${}^* K_{as} = [L \cdot T][H]/[LH] \quad (6)$$

$${}^* \beta_{LT} = K_a \cdot \beta_{LT} \approx {}^* K_{as}/c_T \Rightarrow {}^* K_{as} = {}^* \beta_{LT} \cdot c_T. \quad (7)$$

The equilibrium constant for the formal acid-base equilibrium, ${}^* K_{as}$, which is determined in graphical or numerical interpretation of the absorbance curves, is thus only the conditional equilibrium constant, valid only for the given experimental conditions (c_L , c_T , c_X).

Introduction of the relationships for the overall absorbance of the solution A at individual thicknesses of the absorbing layer and the equations for the overall mass balance of all the components of the reaction system c_L , c_T and c_X ,

$$A = \varepsilon_1[LH] + \varepsilon_2[L] + \varepsilon_3[L \cdot T] \quad (8)$$

$$c_L = [LH] + [L] + [L \cdot T] \quad (9)$$

$$c_T = [L \cdot T] + [T] + [T \cdot X] \approx [L \cdot T] + [T] \quad (10)$$

$$c_X = [T \cdot X] + [X] \approx [X] \quad (11)$$

permits rearrangement of Eqs (7)–(11) to yield the resultant relationships

$$\begin{aligned} A &= c_L \cdot \varepsilon'_3 - (A - c_L \cdot \varepsilon_1) [H]/(K_a + {}^* \beta_{LT} \cdot c_T) = \\ &= c_L \cdot \varepsilon'_3 - (A - c_L \cdot \varepsilon_1) [H]/K_a(1 + \beta_{LT} \cdot c_T) \end{aligned} \quad (12)$$

$$\begin{aligned} A &= c_L \cdot \varepsilon_1 + (c_L \cdot \varepsilon'_3 - A) \cdot (K_a + {}^* \beta_{LT} \cdot c_T)/[H] = \\ &= c_L \cdot \varepsilon_1 + (c_L \cdot \varepsilon'_3 - A) \cdot K_a \cdot (1 + \beta_{LT} \cdot c_T)/[H] \end{aligned} \quad (13)$$

or, in logarithmic form,

$$\begin{aligned} \log(A - c_L \cdot \varepsilon_1) / (c_L \cdot \varepsilon_3 - A) &= \text{pH} + \log(K_a + {}^*\beta_{LT} \cdot c_T) = \\ &= \text{pH} + \log K_a + \log(1 + \beta_{LT} \cdot c_T) = \text{pH} + \text{p}K_{as}. \end{aligned} \quad (14)$$

The relationships

$$\begin{aligned} \varepsilon'_3 &= (\varepsilon_2 \cdot K_a + \varepsilon_3 \cdot c_T \cdot {}^*\beta_{LT}) / (K_a + {}^*\beta_{LT} \cdot c_T) = \\ &= (\varepsilon_2 + \varepsilon_3 \cdot c_T \cdot \beta_{LT}) / (1 + \beta_{LT} \cdot c_T) \end{aligned} \quad (15)$$

and

$$K_{as} = K_a + {}^*\beta_{LT} \cdot c_T = K_a(1 + \beta_{LT} \cdot c_T) \quad (16)$$

are also valid in these equations.

These equations are a mathematical description of the geometric shape of the absorbance-pH curves, $A = f(\text{pH})$, in tenside solutions and are formally identical with the equations of the absorbance-pH curves of the reagent alone in the region of dissociation equilibrium (A) in the absence of tenside. They are only expanded by inclusion of expressions with constant quantities c_T , β_{LT} and ${}^*\beta_{LT}$.

The geometric shape of the $A = f(\text{pH})$ curves is also completely identical with those for the dissociation equilibria or any equilibria between two absorbing species with dissociation of a single proton, but the absorbance-pH curves are shifted into the acid region compared to the corresponding curves of the reagent alone in the absence of tenside (Fig. 1).

The positions of the absorbance-pH curves and thus also the dependence of the values of the conditional equilibrium constant of reaction (E) on the overall tenside

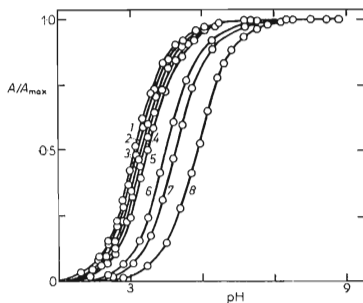


FIG. 1

Dependence of the shift in the normalized absorbance-pH curves of bromocresol green ($c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$) on the concentration of Septonex, $X^- = \text{Cl}^-$, $c_X = 0.01 \text{ mol l}^{-1}$, $1 \cdot 10^{-4} \text{ mol l}^{-1}$ EDTA; Curve $10^4 \cdot c_T$ (mol l^{-1}): 1 5.0, 2 10.0, 3 100.0, 4 3.0, 5 2.0, 6 1.0, 7 0.8, 8 0.0

concentration is controlled by the relationship (cf. Eqs (14) and (16)):

$$\text{pH}_{1/2} = -\log K_{as} = -\log K_a - \log(1 + \beta_{LT} \cdot c_T) \quad (17)$$

The expression for $\text{pH}_{1/2}$ corresponds to the position of the inflection point on the absorbance-pH curve, $A = f(\text{pH})$, for which it holds that $\log(c_{LE_3} - A)/(A - c_{LE_1}) = 0$, and formally corresponds to the value of the dissociation constant. The value of term $-\log(1 + \beta_{LT} \cdot c_T)$ is decisive for the position of the absorbance-pH curve and thus also for the value of $\text{p}K_{as}$. The dependence of $\text{p}K_{as}$ on the overall tenside concentration is depicted in Fig. 2 (right-hand scale) for various stability constants of the ion-associate β_{LT} and a value of the dissociation constant of the reagent of $\text{p}K_a = 3.00$. The individual curves consist of three regions corresponding to different courses of the reaction in dependence on the experimental conditions.

For very stable ion-associates with high stability constants β_{LT} or for the region of sufficiently high overall tenside concentrations, c_T , where the value of expression $\beta_{LT} \cdot c_T$ is much greater than unity ($\beta_{LT} \cdot c_T \gg 1$), the value of $\text{p}K_{as}$ is proportional to the logarithm of the overall tenside concentration, $\log c_T$. The shift in the absorbance-pH curves and the corresponding change in the conditional constant of reaction (E) is then given by the expression

$$\Delta\text{pH}_{1/2} = \Delta\text{p}K = \text{p}K_{as} - \text{p}K_a = -\log \beta_{LT} - \log c_T \quad (18)$$

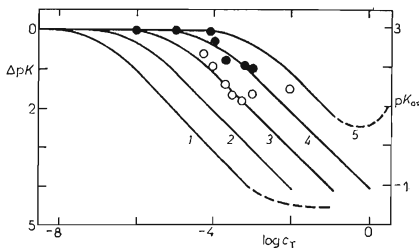


FIG. 2

Dependence of the change in the conditional dissociation constant $\Delta\text{p}K$ (left-hand scale) and the theoretically calculated value of the conditional constant $\text{p}K_{as}$ of Eriochromazurol B ($\text{p}K_a = 3$) (right-hand scale) on the tenside concentration for various values of the stability constant of the ion associate β_{LT} ; Curve β_{LT} : $1 \cdot 10^7$, $2 \cdot 10^6$, $3 \cdot 10^5$, $4 \cdot 10^4$, $5 \cdot 10^3$ for $\text{p}K_a = 3.0$ (right-hand scale) \circ experimental values for $c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$ (bromocresol green) and $c_X = 0.01 \text{ mol l}^{-1} (\text{Cl}^-)$; \bullet data for phenol red, $c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$ and $c_X = 0.015 \text{ mol l}^{-1} \text{Cl}^-$ (ref.¹²)

corresponding to a shift in the absorbance-pH curve along the pH axis by one unit ($\Delta\text{pH}_{1/2} = 1.0$) or a change in $\text{p}K_{\text{as}}$ by one unit on a change in the overall tenside concentration by one order of magnitude. These changes correspond to the linear part of the dependence $\text{p}K_{\text{as}} = f(\log c_{\text{T}})$ in the region $\text{p}K_{\text{as}} \leq 2$ in Fig. 2.

For poorly stable ion-associates of the reagent with the tenside or in the region of low overall tenside concentrations, c_{T} , the value of expression $\beta_{\text{LT}} \cdot c_{\text{T}}$ can be neglected compared to unity ($\beta_{\text{LT}} \cdot c_{\text{T}} \ll 1$). Eq. (17) can then be written in the form

$$\text{pH}_{1/2} = \text{p}K_{\text{as}} = \text{p}K_{\text{a}} - \log(1 + \beta_{\text{LT}} \cdot c_{\text{T}}) \approx \text{p}K_{\text{a}}. \quad (19)$$

The equilibrium constant of reaction (E) and the position of the absorbance-pH curve do not depend on the overall tenside concentration c_{T} and are identical with the value of the dissociation constant and the position of the absorbance-pH curve of the reagent alone, respectively. The dependence of the equilibrium constant $\text{p}K_{\text{as}}$ on the overall tenside concentration is given by expression (19) and the corresponding change in the equilibrium constant is given by the relationship:

$$\Delta\text{p}K = \text{p}K_{\text{as}} - \text{p}K_{\text{a}} = -\log(1 + \beta_{\text{LT}} \cdot c_{\text{T}}) \approx 0. \quad (20)$$

This corresponds to the linear region in the dependence $\text{p}K_{\text{as}} = f(\log c_{\text{T}})$ in the region close to $\text{p}K_{\text{a}} = 3.00$, parallel with the $\log c_{\text{T}}$ axis.

Most real chromogenic reagent-tenside systems lie between these two extremes and do not completely satisfy either of the given assumptions and the value of expression $\beta_{\text{LT}} \cdot c_{\text{T}}$ is comparable with unity. The dependence of the equilibrium constant on the tenside concentration is described by Eq. (17) in the whole range and the corresponding change in the equilibrium constant is given by the relationship:

$$\Delta\text{p}K = \text{p}K_{\text{as}} - \text{p}K_{\text{a}} = -\log(1 + \beta_{\text{LT}} \cdot c_{\text{T}}). \quad (21)$$

This expression corresponds to the nonlinear part of the dependence $\text{p}K_{\text{as}} = f(\log c_{\text{T}})$ in Fig. 2.

The concentration region in the immediate vicinity of the critical micelle concentration of the tenside c_{K} , marked changes occur in the behaviour of the chromogenic reagent-tenside binary system as the shift of the absorbance-pH curves and the corresponding changes in the equilibrium constants are considerably decreased and completely independent of increasing tenside concentration in the region above c_{K} or even have the opposite sign^{10,12}. In this concentration region, the individual molecules (ions) of the tenside begin to associate and high-molecular aggregates, micelles, begin to form; their formation can be expressed by an equation with the corresponding constant β_{T}

$$n T^+ \rightleftharpoons (T_n^+)^{n+} \quad (\beta_T = [T_n]/[T]^n). \quad (22)$$

The number of associated tenside molecules, n , varies from units to several hundred¹⁻³. This equilibrium leads to a marked decrease in the equilibrium concentration of tenside T^+ in the monomeric form, which can be expressed by the relationship

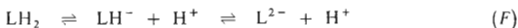
$$c_T = [L \cdot T] + [T] + n[T_n] + [T \cdot X] \approx [T] + n[T_n]; \quad [T] = c_T - n[T_n]. \quad (23)$$

In Eqs (15)–(17), value c_T must be replaced in all the expressions by the value c_T/n and the relationship for the dependence of changes in the equilibrium constant of reaction (E) has the form

$$pK_{as} = pK_a - \log(1 + \beta_{LT}(c_T - n[T_n])) \approx pK_a - \log(\beta_{LT}(c_T - n[T_n])). \quad (23a)$$

The linear part of the dependence $pK_{as} = f(\log c_T)$ is curved in the tenside concentration region close to c_K (see the dashed part of curve 1 in Fig. 2) and the value of pK_{as} attains its limiting value (the curve is parallel with the $\log c_T$ axis) or, for very stable micelle formations, where the bond between the chromogenic reagent and the tenside is broken, the dependence can attain a minimum (maximum) and then monotonically increases (decreases) with increasing tenside concentration (dashed part of curve 5 in Fig. 2).

Similar relationships for the shift of the absorbance-pH curves and changes in the equilibrium constants of reaction (E) can also be derived for a chromogenic reagent dissociating in two steps



with dissociation constants $pK_{a1} = [LH][H]/[LH_2]$ and $pK_{a2} = [L][H]/[LH]$. Assuming that the molecular form of reagent LH_2 does not form an ion-associate with the tenside and the stability of the ion-associate $\{LH^-.T^+\}$ is much greater than that of ion-associate $\{L^{2-}.2T^+\}$, the formation region of the absorbance-pH curve is shifted from the region of the first dissociation LH_2/LH to more acid regions and, on the other hand, in the second dissociation region, LH/L , it is shifted to more alkaline regions. The corresponding equilibrium constants decrease (increase) and the region of predominant existence of the acid-base form LH and its ion-associate $\{LH^-.T^+\}$ is broadened, as indicated on the distribution diagrams for Chromazuril S in the presence of cetylpyridinium in Fig. 3, calculated from experimental data¹⁰.

The completely identical shape of the absorbance-pH curves of the chromogenic reagent in the presence of various tenside concentrations with the curves for the equi-

librium between two absorbing species, reacting with dissociation of a single proton, as demonstrated above, explains why it is possible to use classical graphical and graphical-logarithmic analysis of absorbance curves and numerical interpretation of absorbance curves by the linear or nonlinear least squares method. The molar absorption coefficients ε_1 , ε_2 and ε_3 for the individual absorbing species LH, L^- and $\{L^-, T^+\}$ and the corresponding equilibrium constants of reaction equilibria (A) and (E) can be determined by graphical depiction of dependence $A = f((c_L \varepsilon_3 - A)/[H])$ or $A = f((A - c_L \varepsilon_1) \cdot [H])$. The slopes of the linear dependences then correspond to the expressions for pK_{as} or $1/pK_{as}$ and the intercepts on the A -axis then yield $c_L \varepsilon_1$, or $c_L \varepsilon_3'$, from which the corresponding values ε_3 and β_{LT} can be found using the relationships

$$\varepsilon_3 = (\varepsilon_3' \cdot K_{as} - \varepsilon_2 \cdot K_a) / \beta_{LT} \cdot c_T \quad (24)$$

$$\beta_{LT} = (K_{as} - K_a) / c_T \quad (25)$$

$$\beta_{LT} = \beta_{LT} / K_a \cdot c_T \quad (26)$$

A further way in which the stability constants of the ion-associate of the chromogenic reagent with the tenside can be found employs the dependence of the equilibrium constant of reaction (E) on the overall tenside concentration. Rearrangement of Eq. (17) yields the relationship

$$K_{as}/K_a = 1 + \beta_{LT} \cdot c_T \quad (27)$$

representing the equation of a straight line with slope corresponding to the stability constant of the ion-associate, as the value of dissociation constant K_a can be found separately.

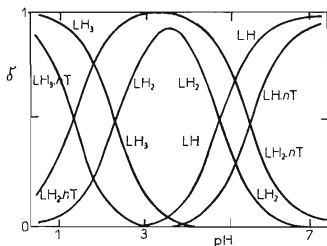


FIG. 3
Distribution diagram for Chromazurol S in the presence of cetylpyridinium bromide (T), $c_T = 5.0 \cdot 10^{-4} \text{ mol l}^{-1}$, in aqueous medium¹⁰

Similarly, if pK_a is known, Eqs (12)–(14) can be rearranged to give a form that permits direct determination of ϵ_3 and β_{LT} . The basic parameters can then be determined in a manner similar to the determination of the equilibrium constants of the complexation reactions.

EXPERIMENTAL

Chemicals and Instrument

Bromocresol green (3',3'',5',5''-tetrabromo-*m*-cresolsulphophthalein, $C_{21}H_{14}O_5SBr_4$, $M_r = 698.1$, further *I*) was the commercial substance (Lachema, Brno, Czechoslovakia) and was purified by repeated recrystallization from alkaline medium acidified with hydrochloric acid to $pH \approx 2$ and subsequent multiple decantation with 0.01M-HCl. The product was dried over solid KOH for 5 days, over silica gel and finally equilibrated with the air. The purity of the substance was controlled with TLC on Silufol_{EP} (Kavalier, Votice, Czechoslovakia). The stock solution of *I* with a concentration of $1.0-2.0 \cdot 10^{-4} \text{ mol l}^{-1}$ was prepared by dissolving a weighed amount of the chromatographically pure substance in several ml of 1M-KOH. After complete dissolution, an aliquot amount of EDTA solution was added to give a final concentration in the measured solution of $1 \cdot 10^{-4} \text{ mol l}^{-1}$ and the solution was diluted to the mark.

Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide, $C_{21}H_{44}O_2N^+Br^-$, $M_r = 422.5$, further *II*) (Slovakofarma, Hlohovec, Czechoslovakia). The stock solution of *II* with a concentration of $0.01-0.001 \text{ mol l}^{-1}$ was prepared fresh before each measurement. Use of older tenside solutions led to marked worsening of the reproducibility of the measurement. A colloidal or crystalline precipitate appeared in the solution and solutions of *II* in the presence and absence of *I* exhibited a marked Tyndall effect.

The other chemicals and solutions, instruments and method used for measuring and treating the experimental data have already been described in an earlier work¹⁰.

RESULTS AND DISCUSSION

The absorption spectra of an aqueous solution of compound *I* with $c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$ and the same solution in the presence of $5 \cdot 10^{-4} \text{ mol l}^{-1}$ *II* are completely identical. Depending on the pH, the absorption spectra exhibit two marked absorption maxima at 420 or 627 and 392 nm. The values of the molar absorption coefficients at the absorption maximum are $1.72 \cdot 10^4$, $4.14 \cdot 10^4$ and $8.4 \cdot 10^3 \text{ mmol}^{-1} \text{ cm}^2$ for aqueous solutions and $1.73 \cdot 10^4$, $4.20 \cdot 10^4$ and $8.6 \cdot 10^3 \text{ mmol}^{-1} \cdot \text{cm}^2$ for solutions in the presence of *II*. The acid-base equilibrium between the yellow protonated acid-base form of the reagent, LH, and the blue anionic form, L^- , is indicated by a sharp isosbestic point at 500 or 503 nm. The absorption spectra at a constant pH value of 5.0 indicate increasing concentration of the blue reagent form L^- with increasing tenside concentration, reflected in increasing intensity of the absorption band around 627 nm.

The dissociation constants of the reagent alone in an aqueous medium for various ionic strengths (Cl^-) were determined by numerical interpretation of the absorbance-

-pH curves at wavelengths in the region of maximum absorbance of both acid-base forms and in their immediate vicinity. The pK_a values, 4.87, 4.71, 4.55 and 4.42 for ionic strengths of 0.01, 0.1, 0.5 and 1.0, respectively, are in good agreement with the literature data²²⁻²⁴.

In the presence of low concentrations of II ($c_T < 8 \cdot 10^{-5} \text{ mol l}^{-1}$) at $c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$, a precipitate of the ion-associate of the reagent with the tenside is formed in solution. The 1:1 ion-associate can readily be extracted into chloroform, which was utilized for the quantitative determination of the anion active tenside by two-phase titration²⁵. At higher II concentrations, the ion associate is solubilized and the solutions are clear or exhibit only a slight Tyndall effect.

The absorbance-pH curves of a solution of I with concentration $1.75 \cdot 10^{-5} \text{ mol l}^{-1}$ in the presence of $0.01 \text{ mol l}^{-1} \text{ HCl} + \text{NaCl}$ are shifted into more acid regions with increasing tenside concentration. This shift stops at $c_T = 5 \cdot 10^{-4} \text{ mol l}^{-1}$ and is reversed during a further increase in the concentration of II (Fig. 1). The value of the molar absorption coefficient in the region of both horizontal parts of the absorbance-pH curves also increases slightly with increasing tenside concentration (c. 5%). Numerical interpretation of the individual absorbance-pH curves yielded the values of the conditional dissociation constants of the acid-base transition LH/L in the range $c_T = 8 \cdot 10^{-5} - 1 \cdot 10^{-2} \text{ mol l}^{-1}$. The corresponding values of the conditional dissociation constants pK_{as} and their changes ΔpK_{as} are listed in Table I. The corresponding changes in the conditional dissociation constants ΔpK of bromocresol green in dependence on the overall tenside concentration are depicted in Fig. 2 by empty circles for a chloride concentration of $c_X = 0.01 \text{ mol l}^{-1}$. Full dots indicate the changes in the conditional dissociation constants ΔpK for phenol red¹² in the presence of $0.015 \text{ mol l}^{-1} \text{ Cl}^-$. It is apparent in both cases that the experimental values of ΔpK for low concentrations of inert electrolyte are in good agreement with the theoretically calculated dependences $\Delta pK = f(\log c_T)$ in a relatively broad Septonex concentration interval ($c_T < 5 \cdot 10^{-4} \text{ mol l}^{-1}$). The value of the stability constants of the corresponding ion-associates with Septonex are of the order of 10^5 .

TABLE I

The values of the conditional dissociation constants of bromocresol green ($c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$) in the presence of $1 \cdot 10^{-4} \text{ mol l}^{-1}$ EDTA and $0.01 \text{ mol l}^{-1} \text{ Cl}^-$ in dependence on the concentration of tenside - Septonex

$10^4 \cdot c_T / \text{mol l}^{-1}$	0.0	0.8	1.0	2.0	3.0	5.0	10	100
pK_{as}	4.87	4.24	4.02	3.44	3.30	3.14	3.23	3.36
ΔpK	0.00	0.61	0.83	1.41	1.55	1.71	1.62	1.49

for I and 10^4 for phenol red. At higher inert electrolyte concentrations, the agreement of the experimental ΔpK value with the theoretical curves is much worse and the concentration range for which this agreement is valid decreases with increasing inert electrolyte concentration. This is probably a result of more intense participation of competing equilibrium (C) than at low electrolyte concentrations.

Depending on the type and overall concentration of inorganic acid anions used for adjustment of the ionic strength of the solution, the absorbance-pH curves of I shift variously into the more acid region. This shift and the values of the conditional dissociation constant of I decrease in the order $Cl^- < SO_4^{2-} < NO_3^- < ClO_4^-$ (see Fig. 4 and Table II). A white crystalline precipitate of the ion-associate of Septonex with ClO_4^- ions is formed in the presence of low concentrations of ClO_4^- ions in solution and the absorbance-pH curve of I and the corresponding pK_{as} values agree with the absorbance-pH curve and pK_a value of the reagent in the absence of Septonex. Similarly, the precipitate of the ion-associate of Septonex with NO_3^- and SO_4^{2-} ions begins to be formed at NO_3^- or SO_4^{2-} concentrations greater than 0.4 mol l^{-1} or 0.6 mol l^{-1} , respectively.

The shift in the absorbance-pH curves and the corresponding changes in the conditional dissociation constants for the given inorganic acid anion decrease with increasing anion concentration, as is apparent from Fig. 5 for $c_{Cl^-} = 0.01 - 1.00 \text{ mol l}^{-1}$.

TABLE II

The values of the conditional dissociation constants of bromocresol green ($c_L = 1.75 \cdot 10^5 \text{ mol l}^{-1}$) in medium containing $5 \cdot 10^{-4} \text{ mol l}^{-1}$ Septonex or cetylpyridinium bromide and $1 \cdot 10^{-4} \text{ mol l}^{-1}$ EDTA in dependence on the type and concentration of inert electrolyte X^-

X^-	$c_X, \text{ mol l}^{-1}$							
	0.01	0.05	0.10	0.15	0.20	0.30	0.50	1.00
Cl^-	3.14	—	3.79	—	4.05	—	4.31	4.46
Cl^-^a	2.85	—	3.52	—	3.79	—	4.06	4.39
NO_3^-	3.35	3.91	4.24	4.35	4.42	4.53	—	—
SO_4^{2-}	3.37	3.50	3.56	—	3.68	—	3.84	—
ClO_4^-	4.8	—	—	—	—	—	—	—
$Cl : NO_3 \ 2 : 1^b$	—	—	3.82	—	—	—	—	—
$Cl : NO_3 \ 1 : 1^b$	—	—	3.93	—	—	—	—	—
$Cl : NO_3 \ 1 : 2^b$	—	—	4.05	—	—	—	—	—

^a $5.0 \cdot 10^{-4} \text{ mol l}^{-1}$ cetylpyridinium bromide medium; ^b ratio of material amounts of chloride and nitrate at a constant ionic strength of the solution $I = 0.10$.

$\cdot 1^{-1}$ and from Table II for the other anions. This effect was attributed primarily to changes in the overall value of the ionic strength of the solution^{1,3,6,12}. Competitive formation of the ion-associate of anion X^{-} with the tenside (equilibrium C) has a decisive effect on the changes in the acid-base properties. This reaction competes with formation of the ion-associate of the tenside with the reagent, $\{L^{-} \cdot T^{+}\}$, so that the effect of the tenside on changes in the acid-base equilibria of the reagent is smaller in inert electrolyte solutions with greater affinity of the anion for the tenside.

The decisive effect of the kind and overall concentration of anion X^{-} is demonstrated on the example of changes in the conditional dissociation constant of I in the presence of a mixture of Cl^{-} and NO_3^{-} in various concentration ratios ($c_{HCl} = 0.1 \text{ mol l}^{-1}$, $c_{HCl} = 0.067 \text{ mol l}^{-1} + c_{HNO_3} = 0.033 \text{ mol l}^{-1}$, $c_{HCl} = 0.05 \text{ mol l}^{-1} + c_{HNO_3} = 0.05 \text{ mol l}^{-1}$, $c_{HCl} = 0.033 \text{ mol l}^{-1} + c_{HNO_3} = 0.067 \text{ mol l}^{-1}$ and $c_{HNO_3} = 0.1 \text{ mol l}^{-1}$) at a constant sum of the overall concentrations of the anions of both acids and thus also constant value of the ionic strength of the solution, $I = 0.10$. The absorbance-pH curves and corresponding values of the conditional dissociation

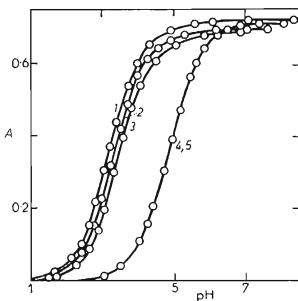


FIG. 4

The effect of the kind of inert electrolyte on the acid-base properties of bromocresol green in the presence of $5.0 \cdot 10^{-4} \text{ mol l}^{-1}$ Septonex(II) $c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{EDTA} = 1.0 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_X = 0.10 \text{ mol l}^{-1}$. Curve X^{-} : 1 Cl^{-} , 2 SO_4^{2-} , 3 NO_3^{-} , 4 ClO_4^{-} , 5 Cl^{-} without II

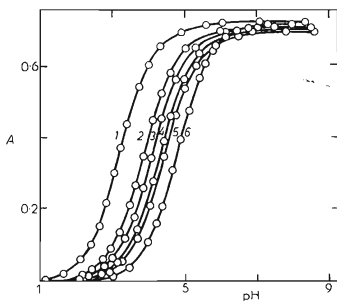


FIG. 5

The effect of the overall concentration of inert electrolyte on the acid-base equilibria of bromocresol green in Septonex medium. $c_L = 1.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{EDTA} = 1 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_T = 5.0 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_X = 0.01$ to 1.00 mol l^{-1} ($X = Cl$) Curve c_X : 1 0.01, 2 0.10, 3 0.20, 4 0.50, 5 1.00, 6 0.01 without II

constant pK_{as} are shifted into the acid region with increasing concentration ratio $c_{Cl^-}/c_{HNO_3^-}$ (see Table II). The changes are, however, less marked than for Chromazurol S and Eriochromazurol B¹⁰.

Association of the dye with the tenside and the effect of further competing equilibria does not formally change the shape of the absorbance-pH curves, confirming the correctness of using classical methods to evaluate the dissociation constants of acid-base indicators. Dissociation constants found in this way are only conditional dissociation constants, that are a function of the kind and concentration of tenside, dissociation constant pK_a of the indicator and stability constant of the ion-associate formed between the reagent molecule and the tenside. These conclusions are generally valid for formation of ion-associates between cationic basic dyes and anionic tensides $\{L^+.T^-\}$, as indicated by the results of study of the interaction of sodium dodecylsulphate and basic dyes of the neutral red, methyl green types, etc²⁶.

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